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PRIORITY DATE CLAIMED
30 SEPTEMBER 1999

TITLE OF INVENTION

NOVEL TRANSITION METAL PHOSPHIDE CATALYSTS

APPLICANT(S) FOR DO/EO/US

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31)
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau)
 - b. ☐ have been communicated by the International Bureau
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3))
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4)
22. ☐ Certificate of Mailing by Express Mail
23. ☐ Other items or information:

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24. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :				CALCULATIONS PTO USE ONLY	
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO				\$1000.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO				\$860.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO				\$710.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)				\$690.00	
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)				\$100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$100.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30				\$130.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	39 - 20 =	19	x \$18.00	\$342.00	
Independent claims	5 - 3 =	2	x \$84.00	\$168.00	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$740.00	
<input checked="" type="checkbox"/> Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				\$370.00	
SUBTOTAL =				\$370.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				\$0.00	
TOTAL NATIONAL FEE =				\$370.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				\$370.00	
				Amount to be:	\$
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a. ☒ A check in the amount of **\$370.00** to cover the above fees is enclosed.

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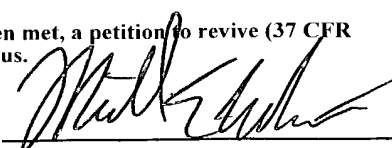
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NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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NOVEL TRANSITION METAL PHOSPHIDE CATALYSTS

This application is based on U.S. Provisional Application No. 60/156,701 filed September 30, 1999 herein incorporated by reference in its entirety.

Background of the Invention

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Field of the Invention

This invention pertains to a catalyst composition and a method for hydrotreating hydrocarbon feedstocks, and more particularly to hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD).

Background Description

10

Phosphorus has been used in combination with transition metals on supports for use in hydrotreating hydrocarbon feedstocks. In these cases, the phosphorus is in the form of an oxide (phosphate) usually incorporated as an additive. From the literature it is understood that the phosphorus can have multiple roles. For example, it can stabilize the surface area of the support, prevent the formation of compounds such as cobalt or nickel aluminate, alter acid-base properties, or aid in the dispersion of the metals in the catalyst.

15

Several references have utilized phosphorus as an oxide component. For example, U.S. Patent Number 4,600,703 describes a catalyst composed of Mo, Ni, and phosphorus oxide deposited on an alumina support and calcined at 450-650 °C. U.S. Patent Number 4,520,128 describes a catalyst composed of a group 6 metal, a group 8 metal, and phosphorus oxide on an alumina support and calcined at 400-600 °C. U.S. Patent Number 4,687,568 describes a catalyst consisting of Ni sulfide supported on a Zr compound to which is added a compound containing P and O. U.S. Patent Number 4,707,246 describes a catalyst containing either Mo, zinc titanate, either Ni or Co

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supported on alumina to which is added a compound containing P and O. In U.S. Patent Number 4,392,985 to a catalyst composed of Mo promoted with Co is added P in the form of orthophosphoric acid, and then calcined at a temperature of at least 750 °F (400 °C). In U.S. Patent Number 4,388,222 to a catalyst composed of Mo promoted with Ni or
5 Co is added P in the form of phosphoric acid, and is then calcined. In U.S. Patent Number 4,632,914 Mo, W, Co and Ni are supported on bauxite and to this is added orthophosphoric acid followed by calcination between 300-600 °C. U.S. Patent Number 4,588,706 and U.S. Patent Number 4,689,314 describe a catalyst constituted of a group 6 metal, a group 8 metal and P in the form of phosphoric acid which is calcined at 400-550
10 °C. WO 9,708,273A1, U.S. Patent Number 4,941,964, and U.S. Patent Number 5,322,616 describe a catalyst comprising an alumina support, a group 8 metal oxide, a group 6 metal oxide, and phosphorus oxide. In U.S. Patent Number 4,743,574 the phosphorus is added to the alumina support to form an aluminum phosphate, and on this are added Co and Mo oxides. U.S. Patent Number 3,755,148, U.S. Patent Number
15 3,755,150, and U.S. Patent Number 3,755,196 describe supported catalysts containing Mo, Ni or Co with P added as orthophosphoric acid.

Several references describe catalyst preparation conditions where the phosphorus is transformed to an oxide. For example, in U.S. Patent Number 4,446,248 a catalyst containing Mo, Ni, and P on alumina is calcined between 975-1025 °F (525 -550 °C). In
20 U.S. Patent Number 4,003,828 a catalyst containing Mo or W and Co or Ni is prepared on a support obtained by cogellation of alumina and phosphorus oxide. U.S. Patent Number 5,021,385 describes a catalyst prepared by adding Mo and Ni and optionally P to a hydrogel of Ti and Zr and calcining between 325-450 °C. U.S. Patent Number

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4,716,141 and U.S. Patent Number 4,738,945 describe a catalyst prepared by adding Ni and either Mo or W with P to an alumina obtained by precipitation and calcining between 300-900 °C. U.S. Patent Number 4,717,705 describes a catalyst prepared by adding Co and either Mo or W with P to an alumina obtained by precipitation and calcining between 300-900 °C. After the calcination step the metals are converted to sulfides by a separate sulfidation step for example at 250-330 °C as described in U.S. Patent Number 4,689,314 or by exposure to a feed containing sulfur. In no case are phosphides formed at the conditions of preparation.

In the cases described above, the phosphorous component in standard catalysts is found in oxidized form, essentially a phosphate compound. This oxidation occurs as a result of calcination (high temperature treatment in air or oxygen). The presence of phosphate in the standard catalysts is well established by nuclear magnetic resonance (NMR) and x-ray photoelectron spectroscopy (XPS) studies. One example, is U.S. Patent Number 5,462,651 which reports the NMR chemical shift for phosphate as occurring between -5 and -30 ppm. In phosphides the NMR chemical shift occurs between +30 and +300 ppm.

Summary of the Invention

The present invention is directed to a catalyst where the phosphorous component is in reduced form, in the form of a phosphide highly dispersed on a high surface area support. The formation of the phosphide on the support is a result of high temperature reduction during preparation of the catalyst. Catalysts prepared in accordance with the present invention produce a highly dispersed catalyst in which the surface area of the metal component is enhanced.

An object of this invention is to provide a transition metal phosphide catalyst highly dispersed on a high surface area support. Another object of the present invention is to provide a transition metal phosphide catalyst for hydrotreating hydrocarbon feedstocks. Further, an object of the present invention is to provide a catalyst material that that is easy to prepare through the reduction of phosphate, and that is easy to regenerate through reduction or by oxidation followed by reduction.

The present invention includes a catalyst comprising a metal phosphide complex having the formula MP_x , where M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and where x ranges from about 0.1 to about 10; and a high surface area support, where the metal phosphide complex is dispersed on the high surface area support. Further, in a preferred embodiment, x may range from about 0.5 and about 3.

The high surface area support may be selected from the group consisting of carbon, silica, alumina, titania, thorina, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof. The metal phosphide complex may be supported on the high surface area support in the range from about 1 to about 40% by weight of complex to support and preferably in the range from about 10 to about 30% by weight of complex to support.

The invention further includes a metal phosphide catalyst comprising a metal phosphide complex having the formula $A_aB_bP_y$, where A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, where the sum of a and b is 1, the ratio of a to b is between about 0.01 and about 100, and y is between about 0.1 and about 10. The ratio of a to b may range from about 0.1 to about 10. Further, the

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ratio of a to b may preferably range from about 0.2 and 5. Further, y may preferably range from about 0.5 and about 3. The metal phosphide complex is dispersed on the high surface area support.

The present invention more generally includes a metal catalyst comprising at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein at least a portion of the one metal is in the form of a phosphide; and a high surface area support wherein the at least one metal and said phosphide are highly dispersed on said high surface area support.

The catalysts of the present invention may also include a promoter selected from the group consisting of the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, boron, carbon, nitrogen, aluminum, sulfur, gallium, germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

Further, the invention includes a method for hydrotreating a hydrocarbon feed comprising the step of exposing the hydrocarbon feed to a catalyst in an atmosphere containing hydrogen, where the catalyst comprises at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein at least a portion of the one metal is in the form of a phosphide; and a high surface area support wherein the at least one metal and said phosphide are dispersed on said high surface area support. The phosphide may have the formula MP_x , where M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and where x ranges from about 0.1 and about 10. Further, x may preferably range from about 0.5 and about 3. The phosphide may have the formula $A_aB_bP_y$, where A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1,

the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 and about 10. The ratio of a to b may preferably range from about 0.1 to about 10. Further, the ratio of a to b may preferably range from about 0.2 to 5, and y may preferably range from about 0.5 to about 3.

5 The invention includes a method of hydrotreating a hydrocarbon feed where the step of exposing the hydrocarbon feed to a catalyst is sufficient to remove nitrogen from the hydrocarbon feed.

 The invention includes a method of hydrotreating a hydrocarbon feed where the step of exposing the hydrocarbon feed to a catalyst is sufficient to remove oxygen from
10 the hydrocarbon feed.

 The invention includes a method of hydrotreating a hydrocarbon feed where the step of exposing the hydrocarbon feed to a catalyst is sufficient to hydrogenate an unsaturated organic compound in the hydrocarbon feed.

 The invention includes a method of hydrotreating a hydrocarbon feed where the
15 step of exposing the hydrocarbon feed to a catalyst is sufficient to hydroisomerize an organic compound in the hydrocarbon feed.

 The method of the present invention may include a hydrocarbon feed selected from the group consisting of middle distillates, kero, naptha, gas oil obtained by catalytic cracking, gas oil obtained by thermal cracking, straight-run gas oil, coker gas oil, vacuum
20 gas oils, heavy gas oils, coal liquids, feeds extracted from tar sands, and feeds extracted from shale.

 Further, the method may include the step of processing the hydrocarbon feed in the presence of the catalyst at a temperature ranging from about 250 to about 450 °C,

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pressure ranging from about 5 to about 250 bar, space velocities ranging from about 0.1 to about 10 hr⁻¹, and H₂/feed ratios ranging from about 1000 to about 15000 scf/barrel.

Further, the invention includes a method for hydrosulfurizing a hydrocarbon feed wherein the feed contains sulfur compounds that include sterically hindered, alkyl substituted heteroaromatic condensed rings. The hydrosulfurization process consists of exposing the hydrocarbon feed to a catalyst, wherein the catalyst comprises at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein at least a portion of the one metal is in the form of a phosphide; and a high surface area support wherein the at least one metal and said phosphide are dispersed on said high surface area support. The phosphide may have the formula MP_x, where M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and where x ranges from about 0.1 and about 10. Further, x may preferably range from about 0.5 and about 3. The phosphide may have the formula A_aB_bP_y, where A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 and about 10. The ratio of a to b may preferably range from about 0.1 to about 10. Further, the ratio of a to b may preferably range from about 0.2 to 5, and y may preferably range from about 0.5 to about 3.

Brief Description of the Drawings

- Figure 1 shows X-ray diffraction patterns of fresh and spent 23 wt% MoP/Al₂O₃.
 Figure 2 shows X-ray diffraction patterns of fresh and spent MoP/SiO₂.
 Figure 3 shows X-ray diffraction patterns of fresh and spent WP/SiO₂.
 Figure 4 shows X-ray diffraction patterns of fresh and spent 8.6 wt% Ni₂P/SiO₂.

Figure 5 shows X-ray diffraction patterns of fresh and spent CoP/SiO₂.

Figure 6 shows X-ray diffraction patterns of fresh and spent Fe₂P/SiO₂.

Figure 7 shows X-ray diffraction patterns of NiMoP₂.

Figure 8 shows the reactivity of phosphides in hydroprocessing.

5 Figure 9 shows the X-ray diffraction patterns of WP before and after reaction.

Figure 10 shows a comparison of conversion of 4,6-dimethyldibenzothiophene.

Detail Description of the Invention

The present invention is directed to a catalyst composition and a method for hydrotreating hydrocarbon feedstocks, more particularly hydrosulfurization (HDS),
10 hydrodenitrogenation (HDN), hydrodeoxygenation, hydroisomerization, and hydrogenation (HYD). The invention further relates to processes for the preparation and use of a catalyst composition.

In general, hydrotreating refers to the removal of sulfur (HDS) and nitrogen (HDN) from hydrocarbon feedstocks. The removal of these components is important for
15 producing clean burning fuels. In addition, it is essential to remove these elements, since the catalysts used in subsequent processing, like cracking, hydrocracking, and reforming, are poisoned by the sulfur and nitrogen.

The present invention provides new types of catalysts for hydrotreating hydrocarbon feedstocks. The catalysts are supported transition metal phosphides, a class
20 of material in which the phosphorus forms a chemical compound with the metal component. The metal source can be quite diverse and includes the ammonium salts, chlorides, nitrates, hydroxides, heteropoly compounds and other species. The transition metals that may be used in the catalyst of the present invention includes, but is not

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limited to, Mo, W, Fe, Co, Ni, V, Nb, Cr, Mn, Ta, and other suitable transition metals.

The catalyst may be prepared according to the formula MP_x where M is a metal and x may range from about 0.1 to about 10. Preferably x ranges from about 0.5 to about 3.

The metals may be combined in various ratios to form multimetallic phosphides according to the formula $A_aB_bP_y$ where A and B are metals and where the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10. Preferably the ratio of a to b ranges from about 0.1 to about 10 and most preferably the ratio of a to b ranges from about 0.2 to 5. Further, y preferably ranges from about 0.5 to about 3. Mixed metal compositions can give rise to diverse substances with potentially very unique properties such as activity, or selectivity for the hydrotreating reactions. Some of the mixed metal composition includes $Mo_aCo_bP_y$, $Mo_aNb_bP_y$, $W_aNi_bP_y$, and the like. It will be evident to those skilled in the art that a wide variety of multimetallic phosphides can be prepared where the catalyst contains three or more metal elements.

The phosphorus source can be similarly diverse, and includes phosphoric acid, phosphorous acid, and the various ammonium hydrogen phosphates. The relative amounts of phosphorus (P) and metal (M) are given by molar percentages of 50 to 300 mol% which correspond to stoichiometries of $MP_{0.5}$ to MP_3 .

The catalysts are in supported form, where the active metal phosphide is present on the support as either small particles or as a surface phase. The metal phosphide may be present on the support as particles ranging from 1nm to about 10 μ m in size.

Dispersing the metal phosphide on the high surface area support increases the surface area of the metal phosphide compared to the bulk form. The phosphides are deposited on

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with the feed. The catalyst is typically formed as spheres or extrudates, which include symmetrical and asymmetrical polylobed particles.

It will be clear to those skilled in the art that there can be a wide number of variations on this method. It should be possible to apply a plurality of impregnating steps, the impregnating solutions containing one or more of the component precursors, or a portion thereof. Instead of impregnating techniques other methods like dipping methods, or spraying methods can be used to deposit the active components on the support. Similarly, there can be a multitude of variations on the mode and order of drying, calcining, and shaping of the catalyst.

It should also be clear to those skilled in the art that there can be a large number of promoters added to the catalysts to enhance their activity, selectivity or stability. These include, but are not limited to, the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, as well as main group elements like boron, carbon, nitrogen, aluminum, sulfur, gallium germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

The catalysts of the present invention have high activity for hydrodesulfurization and hydrodenitrogenation of hydrocarbon feedstocks. The activity, based on an equivalent surface area, is higher than that of a commercial catalyst studied at the same conditions. The conditions are typical of industrial processes and involve high temperature and pressure. The catalyst of the present invention show high stability with no deactivation over a hundred hours of reaction time.

The present catalysts can be used in the hydrotreating of a wide variety of feeds. These include, but are not limited to middle distillates, kero, naptha, gas oil obtained by

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catalytic cracking, gas oil obtained by thermal cracking, straight-run gas oil, coker gas oil, vacuum gas oils, heavy gas oils, coal liquids, and feeds extracted from tar sands or shale. The conventional process conditions are temperatures in the range of 250-450 °C, pressures in the range of 5-250 bar, space velocities in the range of 0.1-10 hr⁻¹, and H₂/oil ratios in the range of 1000-15000 scf/barrel.

Various aspects of the present invention are illustrated in the following examples. The examples are provided for illustration purposes and should not be construed as limiting the scope of the present invention.

Example 1

Preparation and characterization of MoP/Al₂O₃

Ammonium paramolybdate (Aldrich, 95%) and ammonium phosphate (Aldrich, 99%) were dissolved in distilled water and the solution was used to impregnate a γ-Al₂O₃ support (Degussa, Aluminoxid C) to the point of incipient wetness. The moist paste was calcined in air at 773 K for 6 hours, ground with a mortar and pestle, pressed to 4000 psi, broken, and sieved to particles between 650 and 1180 μm for use. The pelletized precursors were placed in quartz u-tube reactors, and heated with linear temperature ramps (heating rate = 5 K min⁻¹) in flowing hydrogen (Airco, 99.999%) to reduce the metal phosphate to metal phosphide. The hydrogen flow was set at 975 cm³ min⁻¹ per gram of precursor loaded and the final temperature was 850 °C. After reduction the product was cooled to room temperature under helium and passivated progressively with 0.1% O₂/He and then 0.5% O₂/He, then exposed to air in the sample tube for 24 hours. The samples were characterized by CO uptake measurements after reduction in hydrogen for 2 hours at 350 °C. The physical characteristics are shown in Table I. X-ray

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diffraction spectra were collected using a Scintag XDS-2000 diffractometer. The physical properties and x-ray diffraction pattern of the material are shown in Figure 1.

Comparison of the XRD patterns of the supported catalysts to a bulk MoP reference from the powder diffraction files (pdf 24-771) shows the presence of supported MoP.

5 Table I. Physical characteristics of MoP/Al₂O₃ catalysts

Sample [†]	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μmol g ⁻¹
Al ₂ O ₃ blank	90.6	-
6.8 wt%	74.8	20.0
12.8 wt%	71.4	30.6
12.8 wt%*	73.7	29.4
22.7 wt%	59.6	28.8
38.9 wt%	48.8	26.3

† Reduced to 850 °C (β = 5 K min⁻¹, s.v. = 1000 sccm g⁻¹) for 2 hours

* Reduced to 750 °C (β = 5 K min⁻¹, s.v. = 1000 sccm g⁻¹) for 2 hours

Example 2

Preparation and characterization of MoP/SiO₂

10 The catalyst was prepared in the same manner as in example 1, except that the support used was SiO₂ (Cabosil L90). The physical properties are listed in Table II and

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the x-ray diffraction patterns of the material are shown in Figure 2. The XRD patterns of the supported catalysts show a large broad feature at 20° , but otherwise the pattern corresponds to that of MoP as shown by the reference.

Table II. Physical characteristics of MoP/SiO₂ catalysts

Sample	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μ mol g ⁻¹
SiO ₂ blank	91	-
MoP/SiO ₂	50	50

5

Example 3

Preparation and characterization of WP/SiO₂

The catalyst was prepared in the same manner as in example 1, except that the precursor used was ammonium paratungstate (Aldrich, 95%), and the support used was SiO₂ (Cabosil L90). The physical properties are shown in Table III below and the x-ray diffraction pattern of the material is shown in Figure 3. The XRD pattern of the supported catalysts show a large broad feature at 20° , but otherwise the pattern corresponds to that of WP as shown by the reference spectrum from the powder diffraction files (pdf 29-1364).

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Table III. Physical characteristics of WP/SiO₂ catalysts

Sample	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μ mol g ⁻¹

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9.4 wt% Ni ₂ P/SiO ₂ †	118	15
12.2 wt% Ni ₂ P/SiO ₂ *	132	29

† Ni:P = 1:1 * Ni:P = 1:2

Example 5

Preparation and characterization of CoP/SiO₂

The catalyst was prepared in the same manner as in example 4, except that the precursor was cobalt nitrate (Aldrich, 99%) and no nitric acid was needed to form a solution. Equimolar quantities of Co and P were used. The final temperature reduction was 690 °C. The physical properties are listed in Table V below and the x-ray diffraction pattern of the material is shown in Figure 5.

Table V. Physical characteristics of CoP/SiO₂ catalysts

Sample	Physical Characteristics	
	Surface Area m ² g ⁻¹	CO Uptake μmol g ⁻¹
CoP/SiO ₂	134	16

Example 6

Preparation and characterization of Fe₂P/SiO₂

The catalyst was prepared in the same manner as in example 4, except that the precursor was iron nitrate (Aldrich, 99.9%) and no nitric acid was needed to form a solution. Equimolar quantities of Fe and P were used. The final temperature of reduction

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NiMoP ₂	-	-
NiMoP ₂ /SiO ₂	153	55

Example 8

Hydrotreating activities of MoP/Al₂O₃ catalysts

Hydrotreating of a model petroleum liquid consisting of quinoline (Aldrich, 99%), benzofuran (Aldrich, 99%), dibenzothiophene (Aldrich, 99%), tetralin (Aldrich, 99%), and tetradecane (Fisher, 99%), was carried out in a pressurized three-phase trickle bed reactor. Analysis was performed with a gas chromatograph (Hewlett Packard, 5890A) on liquid product collected at 2-3 hours intervals. An amount of catalyst corresponding to 70 μ mol of CO sites was loaded to the reactor. To start the reaction catalyst were pretreated in hydrogen at 623 K and 1 atm for 2 hours. The conditions were set to 3.1Mpa (450 psig), a hydrogen flow rate at 150 cm³ min⁻¹ and a liquid feed rate of 5 cm³ min⁻¹. The results of the catalytic tests are listed in Table VIII below.

Table VIII. Hydrotreating activities of MoP/Al₂O₃ catalysts

Sample †	Hydrotreating Performance		
	HDN %	HYD %	HDS %
6.8 wt%	54	31	51
12.8 wt%	52	33	57
12.8 wt%*	62	29	57
22.7 wt%	58	28	53
38.9 wt%	54	33	44

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† Reduced to 1123 °C ($\beta = 5 \text{ K min}^{-1}$, s.v. = 1000 sccm g^{-1}) for 2 hours

* Reduced to 1023 °C ($\beta = 5 \text{ K min}^{-1}$, s.v. = 1000 sccm g^{-1}) for 2 hours

Example 9

Hydrotreating activities of MoP/SiO₂, WP/SiO₂, Ni₂P/SiO₂, CoP/SiO₂, Fe₂P/SiO₂, and

5 NiMoP₂/SiO₂ catalysts

The catalysts MoP/SiO₂, WP/SiO₂, Ni₂P/SiO₂, CoP/SiO₂, Fe₂P/SiO₂, and NiMoP₂/SiO₂ were tested as in example 8. The results are listed in Table IX. In both the difficult HDN reaction and the HDS reaction, the phosphides had substantially higher activity than a reference MoS₂/SiO₂ catalyst.

10 A concern with the use of any catalyst is its stability in the reaction medium. The phosphides were tested for 100 hours and did not display deactivation. Analysis of the products by XRD after reaction revealed that there was no change in bulk crystal structure (Figures 1-6). Furthermore, XPS revealed that only about 2 mol% of sulfur accumulated on the surface of the catalysts after reaction for 100 hours. These results

15 demonstrate that the catalysts are completely stable in a sulfur environment.

Table IX. Hydrotreating activities of phosphide catalysts

Sample	Hydrotreating Performance		
	HDN %	HYD %	HDS %
MoP/SiO ₂	31	45	20
Wp/SiO ₂	40	46	13
Ni ₂ P/SiO ₂ †	14	38	90
Ni ₂ P/SiO ₂ *	80	19	98
CoP/SiO ₂	30	52	30

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Fe ₂ P/SiO ₂	2	11	3
NiMoP ₂ /SiO ₂	34	45	25
MoS ₂ /SiO ₂	11	45	31

† Ni:P = 1:1 * Ni:P = 1:2

Example 10

The catalysts were tested for HDN, HDS, and hydrogenation (HYD) activity in a trickle bed reactor operated at 643 K (370 °C) and 3.1 Mpa (450 psig). These are standard conditions typically used in an industrial hydroprocessing unit. The reactant feed consisted of quinoline (2000 ppm N), dibenzothiophene (3000 ppm S), tetralin (20 wt.%), and tetradecane (balance). An amount corresponding to 30 m² of catalyst was loaded in the reactor.

The results of the phosphide catalyst compared to NiMoS/Al₂O₃ are shown in Figure 8. In the difficult HDN reaction, tungsten phosphide had substantially higher activity than the commercial NiMo catalyst (58% vs 38%), while in HDS nickel phosphide had very high conversion (90% vs. 77%).

The overall activity of the phosphides was superior to or comparable to that of the sulfide. Also very attractive was the fact that the phosphides showed lower hydrogenation activity than the sulfide, indicating a more effective use of hydrogen, and no cracking.

The phosphides were tested for 100 hours and again did not display deactivation. Analysis of the products by XRD after reaction revealed that there was no change in bulk crystal structure (Figure 9). Furthermore, XPS revealed that only about 2 mol% of sulfur

accumulated on the surface of the catalysts after reaction for 100 hours. These results again demonstrate that the catalysts are completely stable in a sulfur environment.

Example 11

A pressing problem in hydrotreating is the removal of sulfur from refractory compounds like alkyl substituted dibenzothiophenes. This is the problem of deep HDS. In this example the conditions were the same as in Example 7 except that the feed contained 4,6-dimethyldibenzothiophene (500 ppm S), quinoline (200 ppm N), and the solvent was hexadecane. The phosphide catalysts tested were $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{NiMoP}_2/\text{SiO}_2$. Comparison was made to a highly optimized commercial Ni-Mo-S/ Al_2O_3 catalyst (Criterion 424) which was sulfided *in situ* at 400 °C in 10% $\text{H}_2\text{S}/\text{H}_2$ before use. The conversions obtained in HDS are shown in Figure 10. The comparison is on the basis of 70 μmol of active sites loaded in the reactor. The sites were titrated by CO chemisorption for the phosphides and low temperature O_2 chemisorption for the sulfide. As shown in Figure 10, the Ni_2P catalyst has higher activity than the commercial catalyst.

15 It will be readily understood by those persons skilled in the art that the present invention is susceptible to broad utility and application. Many embodiments and adaptations of the present invention other than those herein described, as well as many variations, modifications and equivalent arrangements, will be apparent from or reasonably suggested by the present invention and the foregoing description without
20 departing from the substance or scope of the present invention.

Accordingly, while the present invention has been described in detail in relation to its preferred embodiment, it is to be understood that this disclosure is only illustrative and exemplary of the present invention and is made merely for purposes of providing a

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full and enabling disclosure of the invention. The foregoing disclosure is not intended to be construed to limit the present invention or otherwise exclude any other embodiments, adaptations, variations, modifications or equivalent arrangements, the present invention being limited only by the claims and the equivalents thereof.

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6. The catalyst of claim 1 wherein the metal phosphide complex is deposited on the support in the range of about 10 to about 30% by weight complex to support.

7. A metal phosphide catalyst comprising:

5 a metal phosphide complex having the formula $A_aB_bP_y$, wherein A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10; and

10 a high surface area support, wherein the metal phosphide complex is dispersed on the high surface area support.

8. The metal phosphide catalyst of claim 7 wherein the high surface area support is selected from the group consisting of carbon, silica, alumina, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof.

15

9. The catalyst of claim 7 further comprising a promoter selected from the group consisting of the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, boron, carbon, nitrogen, aluminum, sulfur, gallium germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

20

10. The catalyst of claim 7 wherein the ratio of a to b ranges from about 0.1 to about 10.

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11. The catalyst of claim 7 wherein the ratio of a to b ranges from about 0.2 to about 5 and wherein y ranges from about 0.5 to about 3.

12. The catalyst of claim 7 wherein the metal phosphide complex is deposited on the support in the range of about 1 to about 40% by weight complex to support.

13. The catalyst of claim 7 wherein the metal phosphide complex is deposited on the support in the range of about 10 to about 30% by weight complex to support.

10 14. A method for hydrotreating a hydrocarbon feed comprising the step of:
exposing the hydrocarbon feed to a catalyst in an atmosphere containing
hydrogen, wherein the catalyst comprises:
at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni,
Nb, Mo, Ta, and W, wherein at least a portion of said at least one metal is in the form of a
15 phosphide; and
a high surface area support, wherein the metal phosphide complex is dispersed on
the high surface area support.

15. The method of claim 14 wherein the phosphide has the formula MP_x , wherein M
20 is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and
wherein x ranges from about 0.1 to about 10.

16. The method of claim 15 wherein x ranges from about 0.5 to about 3.

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17. The method of claim 14 wherein the phosphide has the formula $A_aB_bP_y$, wherein A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10
18. The method of claim 17 wherein the ratio of a to b ranges from about 0.1 to about 10.
19. The method of claim 17 wherein the ratio of a to b ranges from about 0.2 to about 5 and wherein y ranges from about 0.5 to about 3.
20. The method of claim 14 wherein the step of exposing the hydrocarbon feed to a catalyst is sufficient to remove nitrogen from the hydrocarbon feed.
21. The method of claim 14 wherein the step of exposing the hydrocarbon feed to a catalyst is sufficient to remove oxygen from the hydrocarbon feed.
22. The method of claim 14 wherein the step of exposing the hydrocarbon feed to a catalyst is sufficient to hydrogenate an unsaturated organic compound in the hydrocarbon feed.

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33. The catalyst of claim 29 wherein the metal phosphide complex is deposited on the support in the range of about 10 to about 30% by weight complex to support.

34. A process for hydrodesulfurizing a hydrocarbon feed containing sulfur

5 compounds comprising the step of:

exposing the hydrocarbon feed to a catalyst, wherein the catalyst comprises:

at least one metal selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein at least a portion of said at least one metal is in the form of a phosphide; and

10 a high surface area support, wherein the metal phosphide complex is dispersed on the high surface area support.

35. The method of claim 34 wherein the phosphide has the formula MP_x , wherein M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and

15 wherein x ranges from about 0.1 to about 10.

36. The method of claim 35 wherein x ranges from about 0.5 to about 3.

37. The method of claim 34 wherein the phosphide has the formula $A_aB_bP_y$, wherein

20 A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a to b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10

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38. The method of claim 37 wherein the ratio of a to b ranges from about 0.1 to about 10.

39. The method of claim 37 wherein the ratio of a to b ranges from about 0.2 to about 5 and wherein y ranges from about 0.5 to about 3.

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(54) Title: NOVEL TRANSITION METAL PHOSPHIDE CATALYSTS

(57) **Abstract:** There is provided a transition metal phosphide catalyst that is active for hydrotreating hydrocarbon feedstocks. The catalyst comprises a transition metal phosphide complex supported on a high surface area support. The high surface area support may be selected from the group consisting of carbon, silica, alumina, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites and combination thereof. The transition metal phosphide complex may include a mixed metal phosphide complex. The catalyst comprises a metal phosphide complex having the formula MP_x , where M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and where x is between about 0.1 and about 10; and an oxide support, where the metal phosphide complex is dispersed on the high surface area support. Further, the catalyst comprises a metal phosphide catalyst comprising a metal phosphide complex having the formula $A_aB_bP_y$, where A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, where the sum of a and b is 1, the ratio of a to b is between about 0.01 and about 100, and y is between about 0.1 and about 10; and an oxide support, where the metal phosphide complex is dispersed on the high surface area support. Further, there is provided a method for hydrotreating a hydrocarbon feed using a transition metal phosphide catalyst. A method for hydrodesulfurization, including deep hydrodesulfurization, using the above catalysts is also described.

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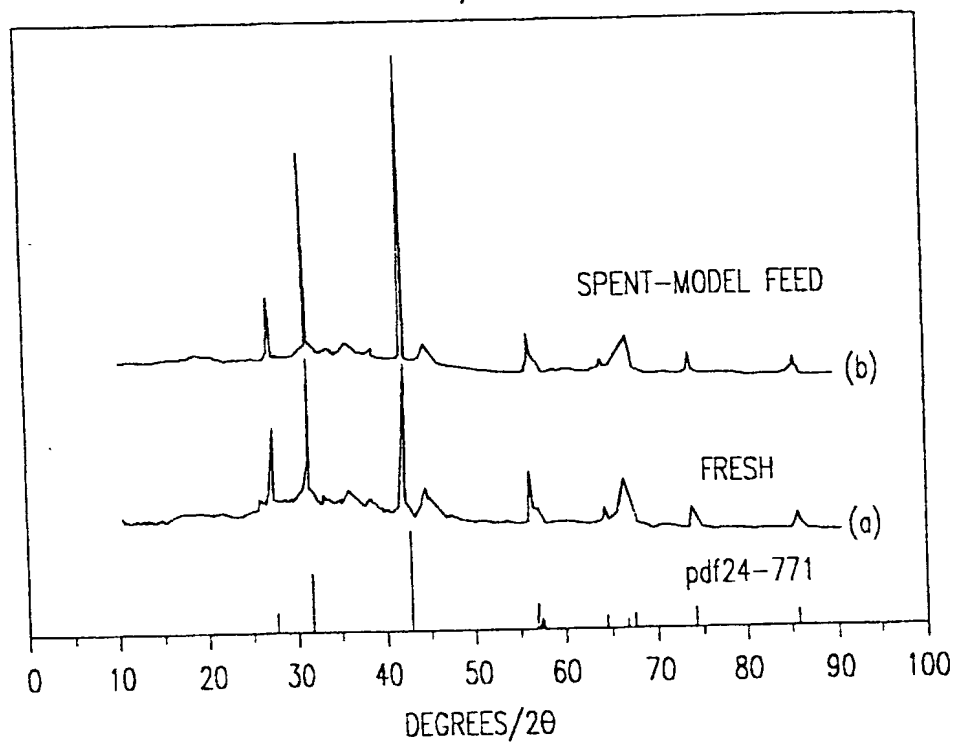


FIG. 1

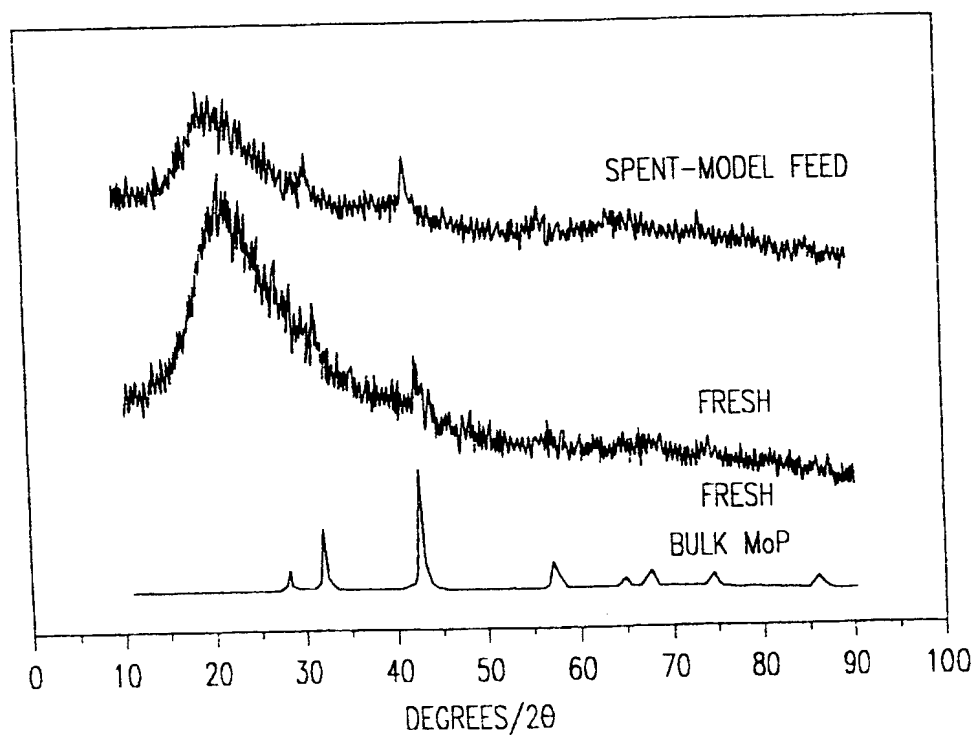


FIG. 2

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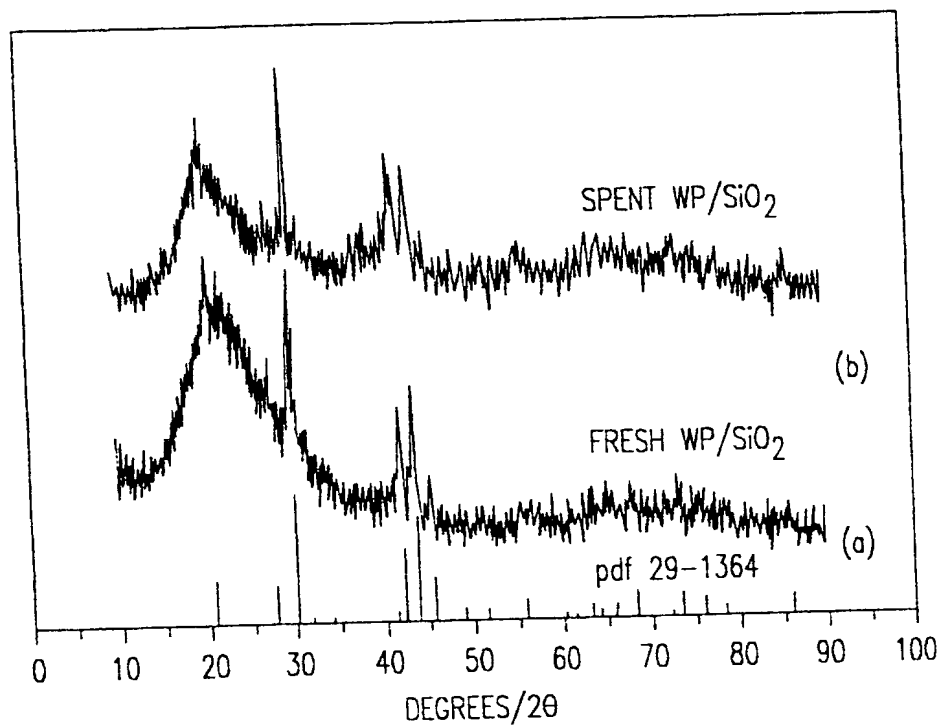


FIG. 3

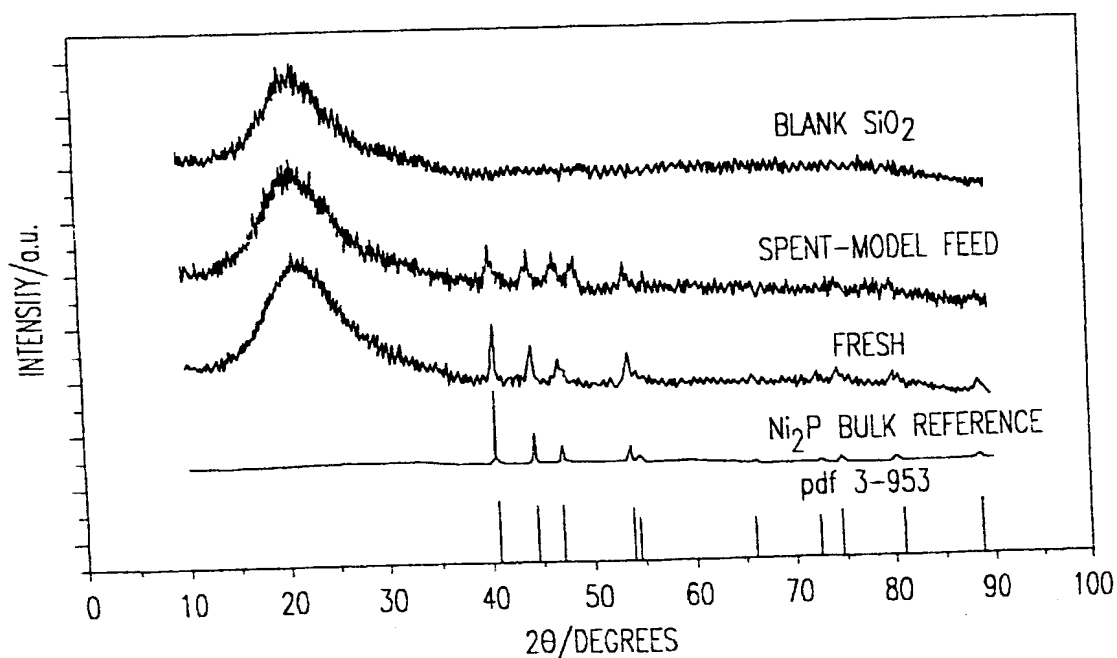


FIG. 4

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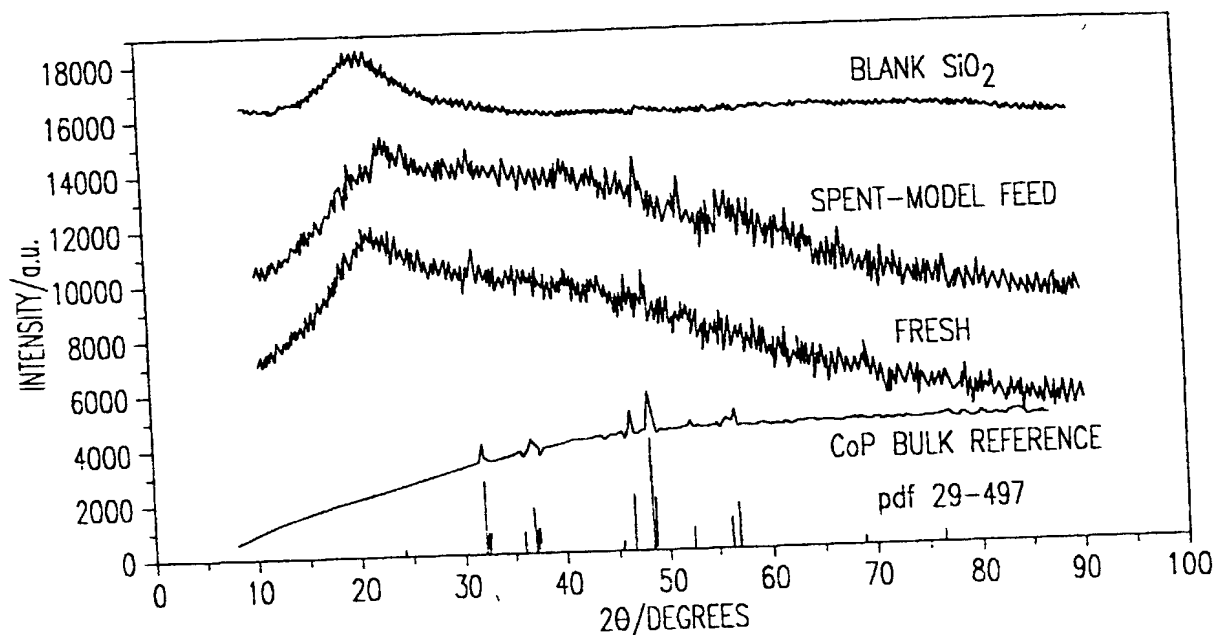


FIG. 5

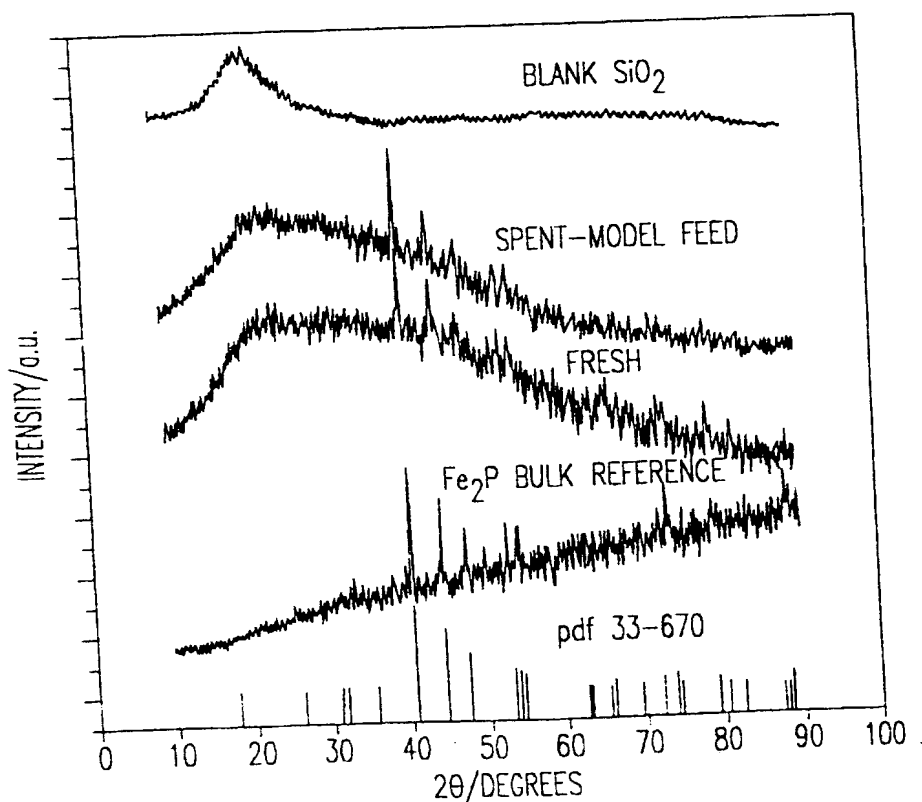


FIG. 6

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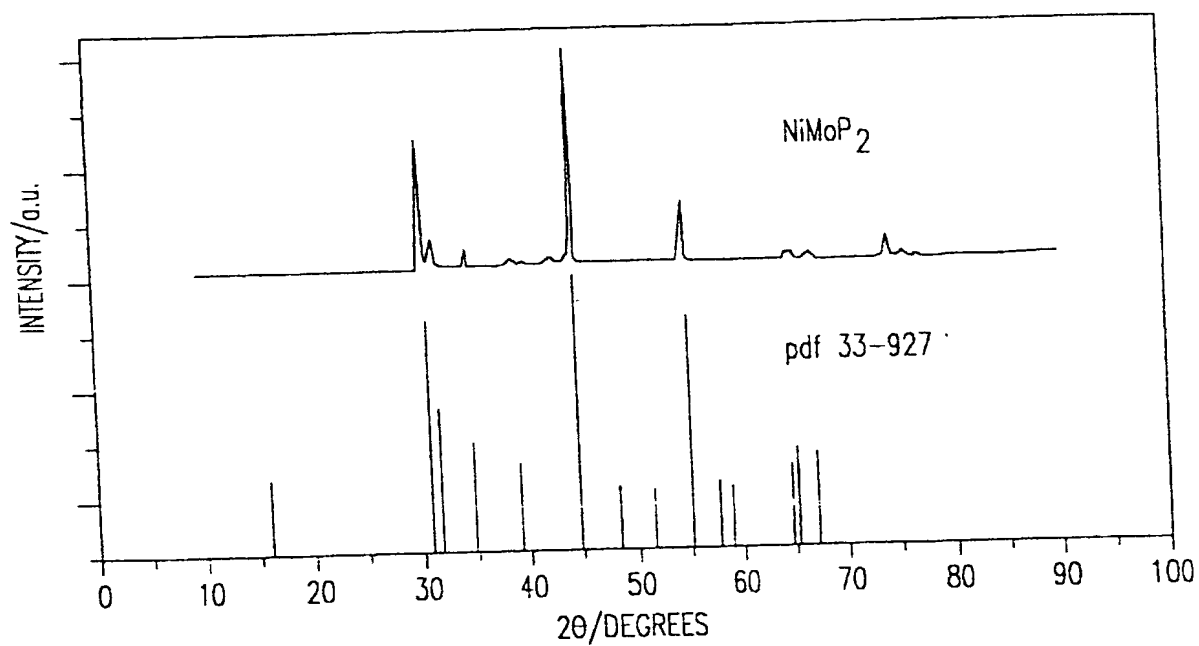


FIG. 7

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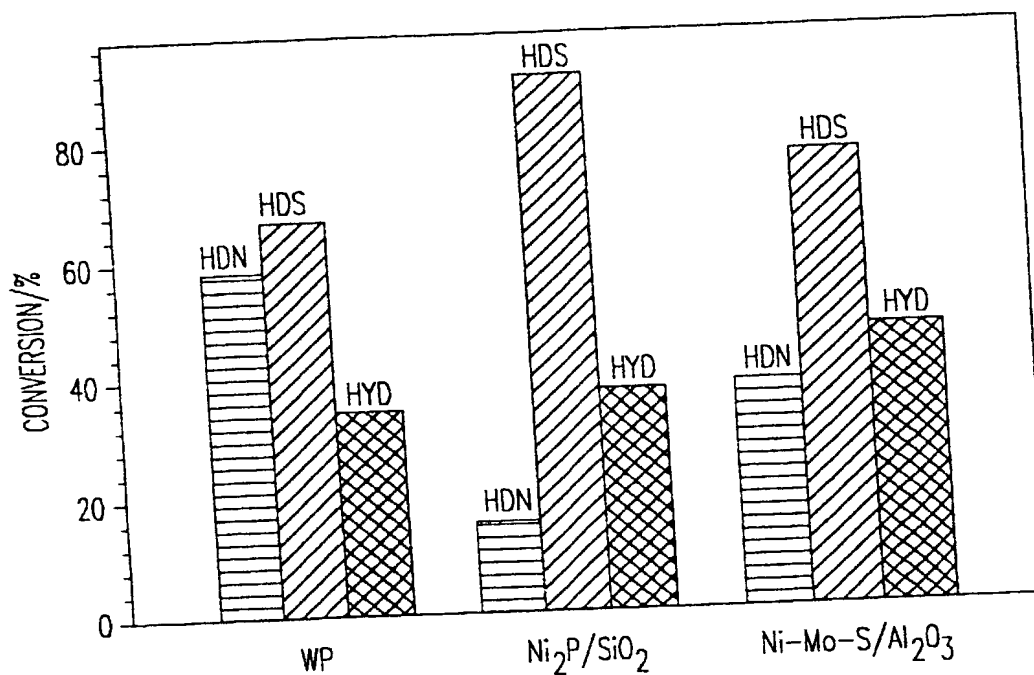


FIG. 8

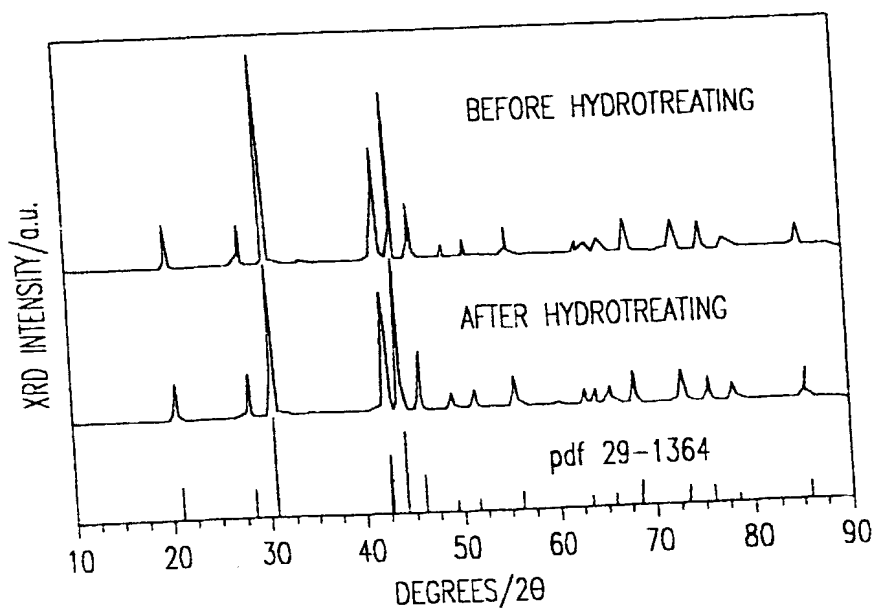


FIG. 9

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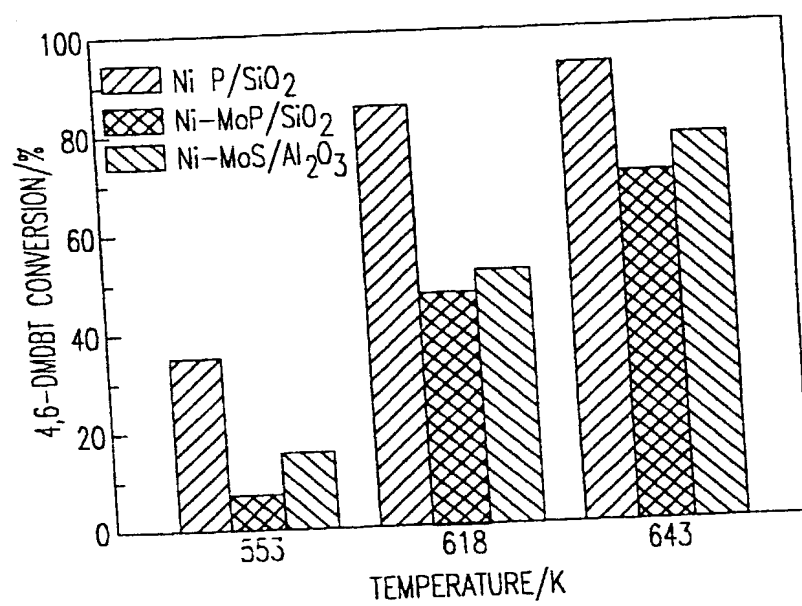


FIG. 10

Docket : 07820001AA

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor
(if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the
invention entitled

NOVEL TRANSITIONAL METAL PHOSPHIDE CATALYSTS

the specification of which:

(check one) ☐ is attached hereto
☒ was filed on March 29, 2002
as Application Serial No. 10/089,515
and was amended on

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56*

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)		priority Claimed
(Appl. No.)	(Country)	(Filing date)
<u>PCT/US00/2663</u>	<u>PCT International</u>	<u>28 September 2000 YES</u>

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status: patented, pending, abandoned)
<u>60/156,701</u>	<u>September 30, 1999</u>	<u>Inactive Provisional</u>

and any continuation applications thereof currently pending.

4
Power of Attorney: As a named inventor, I hereby appoint Michael E. Whitham, Reg. No. 32,635, Marshall M. Curtis, Reg. No. 33,138, Clyde R Christofferson, Reg. No. 34,138, and C. Lamont Whitham, Reg. No. 22,424, as attorneys and/or agents to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. All correspondence should be directed to Whitham, Curtis & Christofferson, P.C., 11491 Sunset Hills Road, Suite 340, Reston, Virginia 20190. All telephone calls should be directed to Michael E. Whitham at 703-787-9400.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Docket: 07820001AA

p-00

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Inventor's Signature Shigeo T. Oyama Date June 28, 2002

Residence 504 Cedar Orchard Drive, West, Blacksburg, Virginia 24060 VA

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e of Federal Regulations, § 1.56:

(a) A patent by its very nature is affected with a public interest. The public interest is best served, and the most effective patent examination occurs when, at the time an application is being examined, the Office is aware of and evaluates the teachings of all information material to patentability. Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith toward the Patent and Trademark Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclose information exists with respect to each pending claim until the claim is canceled or withdrawn from consideration, or the application becomes abandoned.

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